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TITLE: PARTITION COEFFICIENTS OF BIPHENYL AND NAPHTHALENE BETWEEN 1-OCTANOL AND WATER

LAB. CODE LETTERS AND REPORT NUMBER

Wide discrepancy between the log P values for biphenyl reported by Hansch and those by Garner (AL 25-731) have been shown to be caused by volatilization of biphenyl from the separated aqueous layer before analysis by the latter chemist.

Analysis by a corrected technique gave log P for biphenyl = 4.17 ±0.03, corroborating Hansch (4.10), and log P for naphthalene = 3.59 ±0.05.

ISSUED TO			
ATTENTION OF	DEPARTMENT	ATTENTION OF	DEPARTMENT

PARTITION COEFFICIENTS OF BIPHENYL AND NAPHTHALENE BETWEEN 1-OCTANOL AND WATER

EXPERIMENTAL

Reagents

The biphenyl used was Eastman ACS grade 99.8% pure by differential scanning calorimetry; the naphthalene was crystallized 3 times from 95% ethanol, MP 79.6-80.1°C. The octanol used was Eastman #871 saturated with water. The water used was saturated with octanol. The methanol was Burdick and Jackson distilled grade.

Apparatus

International Centrifuge model SBV equipped with a multispeed attachment capable of operation up to 20,000 rpm. Cary recording spectrophotometer model 14.

Procedure

Solutions of the sample in octanol were prepared by accurately weighing the samples into 25-ml volumetric flasks and making to volume with octanol; the solutions had concentrations of 20.00 and 30.00 mg/ml.

Partitioning was done by adding 200 ml of water and 20.0 ml of sample solution to 8-oz. french square narrow-mouth bottles which were previously cleaned and dried. The bottles were closed with polyseal caps and shaken from 4-6 hours on a Eberbach reciprocating tray shaker operating at about 150 cycles per minute. Bottles were shaken lengthwise on their sides, then placed upright for 2 to 10 days to allow the phases to separate.

The clear octanol layer was carefully removed by means of pipet and medicine dropper and transferred to a small bottle for subsequent analysis. The analysis of the organic layer was performed by removing a 20- to 50-µl aliquot using a 50-µl syringe and transferring the aliquot to a 100-ml volumetric flask. The flask was made to volume with methanol and the absorbance of the solution determined at the absorption peak in 1-cm quartz cells. Standard solutions were prepared in the same manner using the same syringe and the unpartitioned portion of the octanol sample solution. The absorptivity of the standard biphenyl in octanol solution was 111 ml mg⁻¹cm⁻¹ at 247 nm. The value for the standard naphthalene in octanol was 43.2 ± .3 at 274 nm.

Aliquots of the cloudy aqueous layer were carefully removed by means of a volumetric pipet. The tip of the pipet was covered with wet cotton to repel any of the octanol layer which may still be present. The aliquots were then centrifuged for various times. Glass tubes were used at 1500 rpm and stainless steel tubes at 10,000 rpm. The centrifuged liquid was then carefully transferred to a 1, 2.5 or 5-cm. cell and the absorbance recorded from 230 to 350 nm. The concentration of sample in the water was then determined from its absorption peak at 248 or 276 nm. Standard solutions of sample in water were prepared by dissolving an accurately weighed (microbalance) portion of sample in 25 ml of methanol followed by dilution to one liter volume in water. The absorptivity of the standard biphenyl in water was 107 ±1 ml/mg/cm at 248 nm (average of three trials); the value for naphthalene in water was 36.6 at 276 nm (one trial).

The partition coefficients were calculated in the usual manner. The concentration of sample in the organic layer was divided by the concentration of sample in the aqueous layer. The results are summarized in Table 1. The organic layer analyzed the same before and after the partitioning (30.0 and 40.0 mg/ml).

DISCUSSION

The aqueous layer was centrifuged in the absence of the organic layer except for the four trials listed in the table. Apparently a loss of sample does occur under these conditions despite the fact that the concentration of sample in the water is well below the solubility concentration. The experimental plan was to centrifuge for 15-minute intervals until the concentration leveled off at a constant value. As can be seen from the table, this result was never achieved and it appears that the concentration would eventually reach 0 if the solutions were centrifuged long enough. In every case the centrifuged solutions were crystal clear, or at worst, very slightly hazy to the eye. From the results listed in Table 1 it appears that the previously reported work of Garner (1) is in error, his high values being obtained by volatilization of biphenyl from the water layer. The value from the present work (based on analyses of aqueous layer at earliest clarification) corroborate the Hansch data.

cpd.	log P	
	found	literature
Biphenyl	4.17 ±0.03	4.10 (2)
Naphthalene	3.59 ±0.05	3.37 (4)

Table 1

Sample	Initial Conc. Octanol Layer mg/ml	Treatment of Aqueous Layer	log P
Biphenyl	30.0	filtered, not centrifuged (hazy)	4.044
Biphenyl	30.0	15 min. at 1500 rpm (clear)	4.204*
Biphenyl	30.0	30 min. at 1500 rpm (clear)	4.262
Biphenyl	30.0	45 min. at 1500 rpm (clear)	4.543
Biphenyl	30.0	5 min. at 10,000 rpm (clear)	4.237
Biphenyl	30.0	10 min. at 10,000 rpm (clear)	4.319
Biphenyl	30.0	15 min. at 10,000 rpm (clear	4.413
Biphenyl	30.0	10 min. at 10,000 rpm with organic layer	4.157*
Biphenyl	40.0	filtered, not centrifuged (hazy)	4.052
Biphenyl	40.0	15 min. at 1500 rpm (clear)	4.150*
Biphenyl	40.0	30 min. at 1500 rpm (clear)	4.242
Biphenyl	40.0	45 min. at 1500 rpm (clear)	4.352
Biphenyl	40.0	5 min. at 10,000 rpm (clear)	4.256
Biphenyl	40.0	10 min. at 10,000 rpm (clear)	4.387
Biphenyl	40.0	15 min. at 10,000 rpm (clear)	4.485
Biphenyl	40.0	10 min. at 10,000 rpm with organic layer	4.171*
Biphenyl	40.0	45. min. sample after standing 5 days	5.377
Naphthalene	30.0	5 min. at 10,000 rpm (clear)	3.578*
Naphthalene	30.0	10 min. at 10,000 rpm (clear)	3.714
Naphthalene	30.0	15 min. at 10,000 rpm (clear)	3.888
Naphthalene	30.0	10 min. at 10,000 rpm with organic layer	3.565*
Naphthalene	40.0	5 min. at 10,000 rpm (clear)	3.637*
Naphthalene	40.0	10 min. at 10,000 rpm (clear)	3.731
Naphthalene	40.0	15 min. at 10,000 rpm (clear)	3.940
Naphthalene	40.0	10 min. at 10,000 rpm with organic layer	3.591*

* Values averaged to obtain reported log P.

REFERENCES

1.

2. Hansch, C., average of 6 determinations from letter to Neely, June 10, 1971.

3.

4. Hansch, C., and Fagita, T., J. Am. Chem. Soc. 66, 1616 (1964).

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